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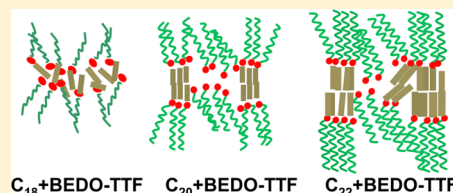
Structure and Electrical Conductivity of Hybrid Langmuir–Blodgett Films from BEDO-TTF and Fatty Acid

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S Supporting Information

ABSTRACT: Conducting Langmuir–Blodgett films are one of the candidates for molecular electronics. We investigated the structural and electrical properties of Langmuir–Blodgett films built up as a mixed molecular system of bis-(ethylenedioxy)tetrathiafulvalene, in short BEDO-TTF, and fatty acid, as a function of (a) the alkyl chain length of the fatty acid and (b) the fatty acid: BEDO-TTF molar ratio in the starting solution from which the Langmuir film is prepared. The Langmuir–Blodgett films deposited from mixtures with molar ratio 1:2 showed better quality in terms of crystallinity and electrical conduction. Moreover, LB films with longer alkyl chain fatty acids were better ordered even at lower molar ratio.



INTRODUCTION

Organic thin films with conducting and semiconducting properties are of growing interest due to their potential for application in molecular-based electronic and optoelectronic devices.^{1–4} Few nanometer thick organic conducting films are promising candidates for applications such as sensors, solar cells, transistors, and light emission diodes.^{5–8} Work on molecular electronics forms an important step in the miniaturization of devices down to the nanometer scale, and hence reliable protocols for the fabrication of such thin structures are desirable. For this purpose, the Langmuir–Blodgett technique has proved to be a very convenient platform that not only provides precise control over layer-by-layer deposition and molecular orientation but also offers the possibility to prepare multilayer structures with varying layer composition. In this way homogeneous functional films of nanometer thickness can be obtained on almost any kind of solid substrate.⁹

Molecular conduction in Langmuir–Blodgett (LB) films dates back to the mid-1980s. In the past two decades, extensive work has been done in producing LB structures with increasing conductivity.¹⁰ Among charge transfer salt-based LB films, the maximum conductivity has been found in systems based on bis(ethylenedioxy)tetrathiafulvalene (BEDO-TTF) with various acceptor molecules.^{11,12} However, in most cases the conductivity of the LB film is several times lower than that of the corresponding bulk organic conductor crystal. This limits the area of application of LB films in molecular electronics. Consequently, the improvement of the structure of the films, the enhancement of the conductivity, and the search for new perspective materials are essential for applications. Molecule-based conduction significantly depends on intermolecular interactions and hence on the arrangement of molecules in the solid phase, which in turn determines the electronic band structure and electronic properties. So the same molecules in

the same oxidation state can give rise to different solid state properties.^{13,14}

The main cause of the degradation of the electrical conductivity of LB films is the polycrystalline structure which leads to thermally activated transport through the intercrystallite potential barriers. Improvement of the crystalline structure is therefore required to achieve highly conductive LB films. This can be achieved by the optimization of various experimental parameters such as deposition pressure, choice of the acceptor molecules, concentration of the molecules, etc. LB films of the mixed molecular system of fatty acid and BEDO-TTF have been shown to exhibit metallic properties.¹¹ The electrical transport properties of such LB films are very sensitive to the mixed valence state of the molecules and their packing in the film structure. Hence, acceptor molecules in the charge transfer complex LB films may influence the electrical transport.

In the present work, LB films composed of amphiphilic fatty acid and BEDO-TTF donor molecules were prepared at various molar ratios of the constituent molecules. The structural and electric transport properties of these films were studied as a function of alkyl chain length of the fatty acid molecules at various molar ratios.

EXPERIMENTAL SECTION

BEDO-TTF was purchased from SYNCHEM. The three fatty acids steric acid ($\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2\text{H}$, called C_{18} in the following), arachidic acid ($\text{C}_{20}\text{H}_{40}\text{O}_2$, called C_{20} in the following), and behenic acid ($\text{C}_{22}\text{H}_{44}\text{O}_2$, called C_{22} in the following) as well as all other chemical reagents of analytical grade were purchased from Aldrich and used as received. The subphase used in the experiments was ultrapure ion free water having a resistivity of greater than 18 $\text{M}\Omega\cdot\text{cm}$ obtained by

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passing double distilled water through the filtering and deionizing columns of a Milli-Q Millipore unit. Surface pressure–molecular area (Π – a) isotherm measurements and deposition experiments were performed using a NIMA Technology thermostated LB trough. Separate solutions of fatty acid (8.22×10^{-4} mol/L) and BEDO-TTF (7.4×10^{-4} mol/L) in chloroform were mixed at 1: y ($y = 0, 1, 2, 3$) molar ratios prior to being spread on the subphase surface. After evaporation of the solvent, the molecules were compressed at a rate of $30 \text{ cm}^2 \text{ min}^{-1}$ by a movable barrier until a 20 mN/m surface pressure was reached, and this pressure was kept during the whole deposition process. LB films were deposited by vertical dipping of hydrophobic substrates into the subphase at a dipping speed of 5 mm/min. The fatty acid–BEDO-TTF layer was deposited each time the substrate moves across the boundary, which indicates Y-type depositions.¹⁵ Hence, one dipping cycle (dipping the substrate into the subphase and subsequently withdrawing it) results in the deposition of two layers. In the following we do not consider the deposition on the backside of the substrate because all characterization techniques were applied only to the front side of the substrate. A Si/SiO₂ substrate was used for X-ray diffraction and electrical measurements. X-ray diffraction patterns of the films were collected with a Philips PANalytical X'Pert MRD diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$).

A commercial PPMS system (Quantum Design) was employed for electrical resistance measurements as a function of temperature. LB films were deposited on a Si/SiO₂ substrate prefabricated with four Au/Ti electrodes separated by 0.5 mm gaps. The dc four-point probe method was applied by sending a constant current (I , with value chosen between 1.0 nA and 1.0 μ A) through the outer two electrodes and measuring the voltage drop (V) in the inner two. The sheet resistance is then computed using the expression

$$R_s = C \frac{V}{I} \quad (1)$$

where C is the correction factor determined by the geometry of the sample and spacing between the electrodes¹⁶ and amounts to 4.4516 for the present case.

Infrared spectra of the LB films on evaporated gold on mica substrate were measured in reflectance mode with a Bruker IFS 66 v/S vacuum FTIR spectrometer operating at 10^{-2} mbar.

RESULTS AND DISCUSSION

1. Π – a Isotherms. The Π – a isotherms of the C_n + BEDO-TTF mixture at different molar ratios were recorded at a temperature of 21 ± 0.1 °C. The lift-off area was calculated for each isotherm by extrapolating the linear section of the isotherm¹⁷ as shown in the inset of Figure 1 for $C_n = C_{18}$. Each isotherm was measured at least three times, and the resulting lift-off area was reproduced with a maximum variation of $\pm 1 \text{ \AA}^2$. Fatty acid molecules with long alkyl chain spontaneously form islands when are spread over water surface. The area fraction of the free water surface reduces while the number and size of the islands increases upon compression.¹⁸ The lift-off area is determined by the nature and size of these islands. Fatty acid molecules with longer alkyl chains tend to form bigger islands with more compact packing due to their higher melting point, consequently giving a steeper increase in surface pressure with smaller lift-off area upon compression. A monolayer of pure C_{18} molecules showed a clear transition from the liquid to the solid phase (Figure 1) at 25 mN/m. The shape of the isotherm is

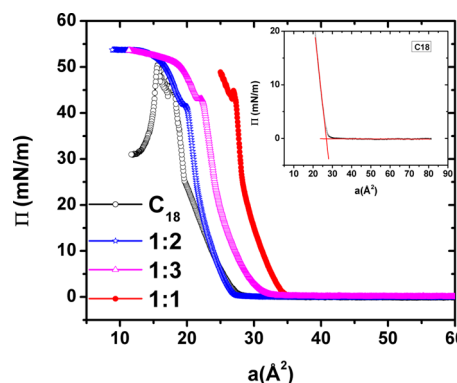


Figure 1. Isotherms measured during compression: surface pressure (Π) vs area per one C_{18} molecule (a) of Langmuir films of pure C_{18} and C_{18} + BEDO-TTF mixtures with different molar ratios. Inset: illustration of the determination of the lift-off area from the Π – a isotherm of a pure C_{18} Langmuir film.

altered for the C_{18} + BEDO-TTF mixture with a larger lift-off area. However, the lift-off area for the C_{18} + BEDO-TTF mixture with 1:2 molar ratio (A_2) is close to that of a pure C_{18} monolayer (A_0) as reported in Table 1. Hence, for this molar

Table 1. Lift-Off Areas in \AA^2 of Langmuir Films of Pure C_n (A_0) and C_n + BEDO-TTF Mixtures Prepared with 1:1 (A_1), 1:2 (A_2), and 1:3 (A_3) Molar Ratios, Where $\Delta_1 = |A_1 - A_0|$ and $\Delta_3 = |A_3 - A_0|$

mixture	A_0	A_1	Δ_1	A_2	A_3	Δ_3
C_{18} + BEDO-TTF	27	34	7	26	30	3
C_{20} + BEDO-TTF	24	28	4	24	30	6
C_{22} + BEDO-TTF	22	20	2	20	27	5

ratio, the area is determined by the lateral packing of the C_{18} molecules. This behavior was first observed by Ohnuki et al. for the C_{22} + BEDO-TTF mixture¹¹ and explained by a bilayer model in which C_{22} form the upper layer and the lower layer comprises the BEDO-TTF molecules. Later, their work on the C_{18} + BEDO-TTF LB films revealed the same isotherm behavior for a 1:1 molar ratio.^{19–21} In the present work Langmuir films of C_{18} + BEDO-TTF mixtures prepared with 1:1 and 1:3 molar ratios exhibited isotherms with larger area/molecule. This implies that the arrangement of molecules at air/water interface is sensitive to the C_{18} :BEDO-TTF molar ratio.

At a surface pressure of 20 mN/m, the occupied area/molecule for C_{20} + BEDO-TTF and C_{22} + BEDO-TTF mixtures with 1:2 molar ratio is close to the occupied area/molecule for pure C_{20} and C_{22} monolayers, respectively (see Figure S1, Supporting Information). However, Δ_1 , which corresponds to $|A_1 - A_0|$, is smaller and Δ_3 , corresponding to $|A_3 - A_0|$, is larger for fatty acids with longer alkyl chains. One may therefore conclude that C_n molecules with longer alkyl chains start forming the bilayer structure at the air/water interface at lower molar ratios. Once the bilayer structure is formed for a particular molar ratio, any further increase of BEDO-TTF concentration in the mixture destroys the Langmuir film. This might be explained considering the lift-off area and area density of fatty acid molecules. A fatty acid with a longer alkyl chain tends to pack more densely and consequently leads to a more compact packing of the BEDO-TTF molecules. This results in a stable C_n + BEDO-TTF

bilayer at the air/water interface via interlayer hydrogen bonding even at smaller concentration of BEDO-TTF molecules.¹⁹

2. X-ray Diffraction Patterns. XRD measurements were carried out at room temperature on 22-layer thick organic films prepared from the C_n + BEDO-TTF mixtures with different molar ratios. Figure 2a shows the XRD pattern of LB films of

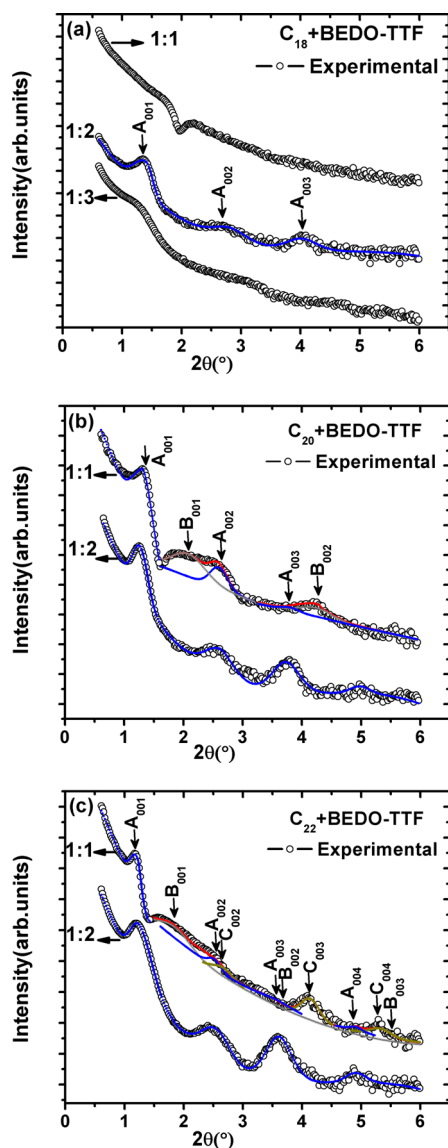


Figure 2. XRD patterns for 22-layer thick LB films deposited from (a) C_{18} + BEDO-TTF, (b) C_{20} + BEDO-TTF, and (c) C_{22} + BEDO-TTF mixtures with different molar ratios; the corresponding fits are also plotted. Conformations A, B, and C are explained in the text.

C_{18} + BEDO-TTF. The XRD pattern of the LB film prepared with 1:1 molar ratio clearly lacked structural order and exhibited a very weak diffraction peak at $2\theta = 1.82 \pm 0.05^\circ$ after background subtraction. The LB film deposited from pure C_{18} also gave the (001) reflection at $2\theta = 1.88 \pm 0.02^\circ$ (see Figure S2). This implies that films prepared from a C_{18} + BEDO-TTF mixture with 1:1 molar ratio have the same repeating unit perpendicular to the film surface as films prepared from pure C_{18} and suggests the absence of a bilayer structure in these C_{18} + BEDO-TTF LB films. However, LB

films deposited with 1:2 molar ratio showed diffraction peaks around $2\theta = 1.34 \pm 0.02^\circ$, $2.67 \pm 0.1^\circ$, and $4.0 \pm 0.2^\circ$. A more detailed analysis of the XRD profile of C_{18} + BEDO-TTF films deposited with 1:2 molar ratio is depicted in Figure 2b. The background was fitted with a polynomial function of fourth order. A linear combination of Gaussian and Lorentzian line shapes with a 75–25% ratio was used for the peak fitting. The size of the repeating unit perpendicular to the film surface (d_A) was calculated from the position of diffraction peaks using the Bragg formula and found to be $d_A = 66 \pm 1 \text{ \AA}$, which is consistent with Y-type LB films. Taking into account the d value of the pure C_{18} LB film ($46 \pm 1 \text{ \AA}$), a thickness of the BEDO-TTF layer of 10 \AA was deduced. For the stacking periodicity with $d_{A(001)} = 66 \text{ \AA}$, all observed diffraction peaks are at expected positions.

LB films deposited from a C_{18} + BEDO-TTF mixture with 1:3 molar ratio showed a significant reduction in structural order. A very weak and broadened (001) peak can be distinguished at $2\theta = 1.32 \pm 0.02^\circ$ after background subtraction (Table 2). Hence, the size of the coherently diffracting unit is smaller in these films than in those deposited from mixtures with 1:2 molar ratio.

Table 2. FWHM₀₀₁ (in deg) of (001) Diffraction Peak for the Conformation A for C_n + BEDO-TTF LB Films

LB films	FWHM ₀₀₁ 1:1 (for C_{20} , C_{22}), 1:3 (for C_{18})	FWHM ₀₀₁ 1:2
C_{18}	0.378 ± 0.003	0.322 ± 0.002
C_{20}	0.331 ± 0.002	0.301 ± 0.002
C_{22}	0.230 ± 0.002	0.332 ± 0.002

Figures 2b and 2c show XRD profiles for 22-layer thick LB films of C_{20} + BEDO-TTF and C_{22} + BEDO-TTF, respectively, at several molar ratios. LB films deposited from a C_{20} + BEDO-TTF mixture with 1:1 molar ratio exhibit the first peak at $2\theta = 1.3 \pm 0.04^\circ$ ($d \sim 70 \text{ \AA}$). If the origin of the periodicity is attributed to C_{20} + BEDO-TTF layered stacking with $d \sim 70 \text{ \AA}$, one would expect (002) and (003) reflections at $2\theta \sim 2.52^\circ$ and 3.83° , respectively. However, both peaks showed a large broadening (FWHM), indicative of multiple conformations.¹⁷ We can analyze the diffraction pattern by assuming two types of conformation: one with a d -spacing of 70 \AA (conformation A) and another one with a d -spacing of 42 \AA (conformation B). Conformation A is most likely composed of C_{20} + BEDO-TTF (where the organic molecules stand upright, almost perpendicular to the film surface), while conformation B consists of C_{20} molecules alone with alkyl chains tilted with respect to the film surface. LB films prepared from mixtures with 1:2 molar ratio gave an improved structure with peaks at $2\theta = 1.26 \pm 0.02^\circ$, $2.52 \pm 0.09^\circ$, $3.83 \pm 0.15^\circ$, and $4.98 \pm 0.3^\circ$. Moreover, for these films the size of the coherently diffracting units is larger as compared to those prepared from mixtures with 1:1 molar ratio as indicated by the smaller FWHM of (001) peak (Table 2).

LB films deposited from C_{22} + BEDO-TTF mixtures with 1:1 molar ratio showed the same type of structural features as observed for C_{20} + BEDO-TTF LB films prepared under the same conditions (Figure 2c). Deconvolution of the diffraction peaks revealed three different conformations: $d_A = 74 \pm 1.5 \text{ \AA}$, $d_B = 48 \pm 1 \text{ \AA}$, and $d_C = 66 \pm 1 \text{ \AA}$. The first and third conformations are assigned to C_{20} + BEDO-TTF molecular layers with almost perpendicular and tilted organic molecules,

respectively, while the second one is most likely composed of C_{20} alone. The (001) diffraction peak of conformation C did not appear in fitting, probably because its intensity is too low. Films prepared with 1:2 molar ratio have a majority phase with $d_A = 74 \pm 1$ Å. However, the (001) peak of conformation A for films prepared from a mixture with 1:1 molar ratio gave smaller FWHM than those deposited from a mixture with molar ratio 1:2. As reported in Table 2, the FWHM for (001) diffraction peak of conformation A decreases when going from C_{18} to C_{20} . This indicates an increase in size of the coherently diffracting unit with the growing alkyl chain length of the fatty acid. From the above observation it is concluded that within the resolution of our XRD data the LB films prepared from a C_n + BEDO-TTF mixture with 1:2 molar ratio have a crystal structure with a single periodicity.

3. FTIR Spectroscopy. To gain further insight into the properties of LB films prepared from C_n + BEDO-TTF mixtures with different molar ratios, FTIR spectra in the frequency range 700–4000 cm^{-1} were collected in reflectance mode. Figure 3 shows the spectra of six-layer thick LB films

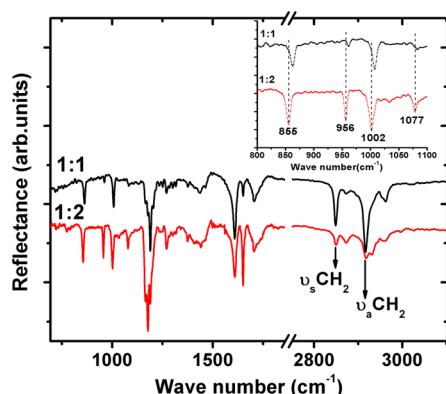


Figure 3. Infrared spectra of six-layer thick LB films deposited from C_{20} + BEDO-TTF mixtures with 1:1 and 1:2 molar ratios. The inset shows the magnified spectra in the low-frequency region.

prepared respectively from C_{20} + BEDO-TTF mixtures with 1:2 and 1:1 molar ratios. Both films showed a series of vibrational bands between 800 and 1200 cm^{-1} , mostly due to vibrations including CO bonds. These absorption features are characteristics of the mixed valence of BEDO-TTF molecules.²² The counteranion in these films is assigned as COO^- of the fatty acid.^{19,21}

The vibrational bands are very sensitive to the average charge on the donor molecule and shift toward lower frequency with increased average charge on the donor, as shown by Moldenhauer et al.²² The LB film prepared from a mixture with 1:2 molar ratio exhibited a higher frequency shift as compared to films prepared from a mixture with 1:1 molar ratio (inset of Figure 3). This confirms the higher degree of charge transfer in the former. The values of the frequency shifts for our LB films were compared to the values observed for different BEDO-TTF-based salts²² where the degree of average charge transfer on the donor molecule ranges from $+0.33 e^-$ to $+0.5 e^-$. In this way the average charge per BEDO-TTF molecule was estimated to amount to $+0.4 e^-$ ($0.33 e^-$) in LB films prepared from a mixture with molar ratio 1:2 (1:1). We therefore suggest the molecular association as $(\text{BEDO-TTF})_2^+(C_n\text{OO}\cdots\text{HOOC}_n)^-$ in the C_n + BEDO-TTF bilayer.¹⁹ However, in the presence of defects, the average charge on a

BEDO-TTF molecule determined from the frequency shift of the vibrational bands in the FTIR spectrum becomes smaller due to the contribution of less conducting or insulating regions (e.g., insulating grain boundaries, etc.). LB films prepared from a mixture with 1:1 molar ratio possess a higher number of structural defects including the insulating pure fatty acid blocks in between the BEDO-TTF stacks and hence showed smaller value of average charge on a BEDO-TTF molecule.

Another remarkable feature in the IR spectra is the lower intensity of symmetric (ν_s) and antisymmetric (ν_a) stretching modes of CH_2 in the LB film deposited from a mixture with 1:2 molar ratio as compared to the one prepared from a 1:1 molar ratio mixture. This intensity decrease indicates that the fatty acid molecules are standing up straight, almost perpendicular with respect to the film surface in LB films prepared from a 1:2 molar ratio mixture.

From the above observations based on the Π - a isotherms, X-ray diffraction data, and FTIR results, a schematic view of the two-layer-thick LB films (obtained from one dipping cycle) can be inferred for what concerns the intercalation of the BEDO-TTF molecules. The resulting structural models for different concentrations and alkyl chain lengths are shown in Figure 4.

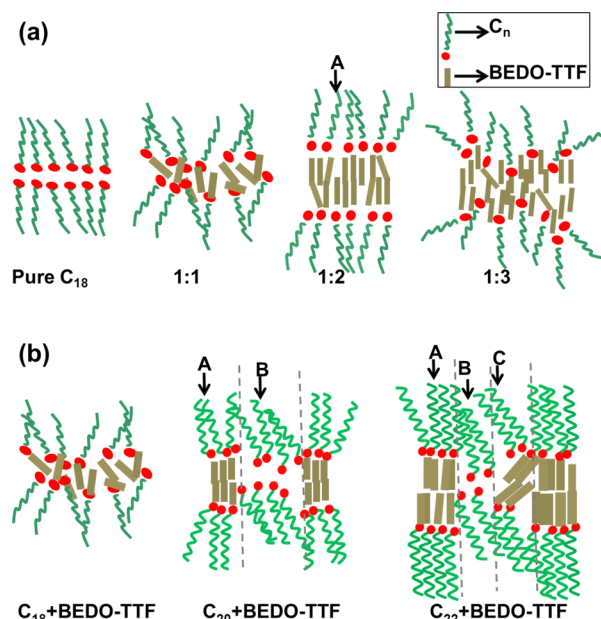


Figure 4. Structural models of the double layers (obtained from one dipping cycle) in Langmuir–Blodgett films deposited from (a) C_{18} + BEDO-TTF mixtures with different BEDO-TTF concentration and (b) C_n + BEDO-TTF mixtures with 1:1 molar ratio but different alkyl chain length, as deduced from isotherm, XRD, and FTIR study. Conformations A and C consist of C_n + BEDO-TTF bilayers with almost perpendicular and tilted organic molecules, respectively, while conformation C is composed of C_n alone.

LB films prepared from a C_n + BEDO-TTF mixture with 1:1 molar ratio exhibit structural defects and multiple conformations that are more pronounced in fatty acids with shorter alkyl chain. On the other hand, LB films prepared from a mixture with 1:2 molar ratio showed a homogeneous crystal structure with a single periodicity. It is important to note that the fatty acid to BEDO-TTF molar ratio in the C_n + BEDO-TTF bilayer remains 1:1 regardless of the starting concentration of mixture, which implies that the in-plane area occupied by one BEDO-

TTF is roughly equal to that of one fatty acid molecule in film structure.²³

4. DC Sheet Resistance of LB Films. Figure 5 shows the temperature variation of the dc sheet resistance (R_s) of the 22-

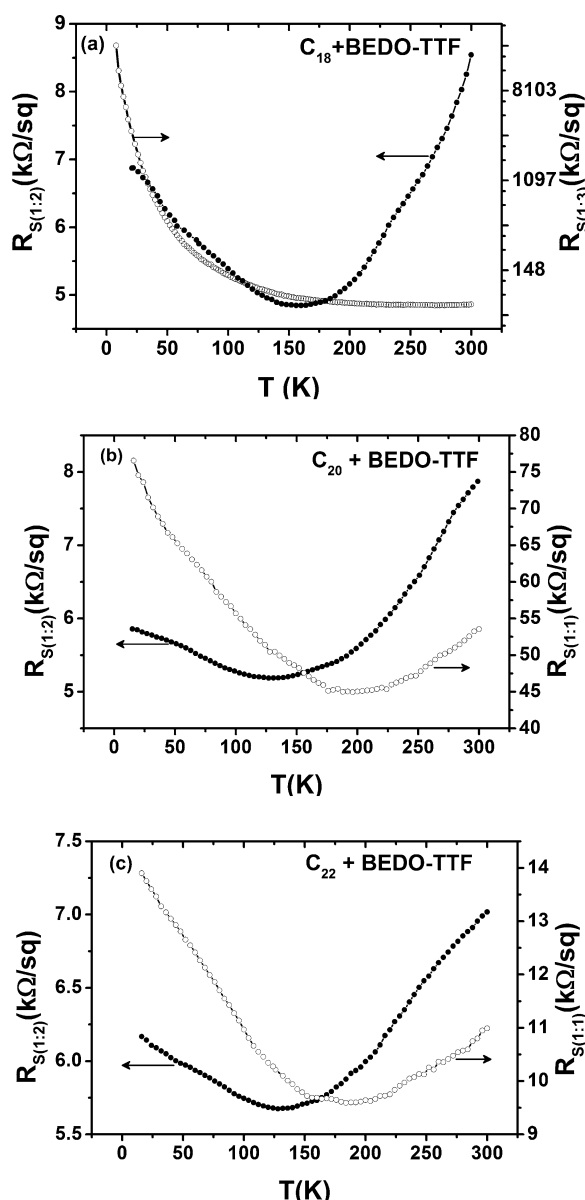


Figure 5. Sheet resistance as a function of temperature of LB films deposited from (a) C_{18} + BEDO-TTF, (b) C_{20} + BEDO-TTF, and (c) C_{22} + BEDO-TTF mixtures with different molar ratios as indicated in the label of the y-axis.

layer thick LB films prepared from C_n + BEDO-TTF mixtures with different molar ratios. A previous study on mixed LB films of BEDO-TTF and C_{18} molecules prepared with a 1:1 molar ratio reported a metallic behavior for $T > 120$ K. However, the resistivity of these films showed a logarithmic increase below 120 K.^{20,21} In the present work, the LB films prepared from C_{18} + BEDO-TTF mixtures with a 1:1 molar ratio were found to be insulating at room temperature. Conducting properties appeared for films deposited from mixtures with a 1:2 molar ratio. They showed metallic character for $T > 150$ K. However, the R_s started increasing with decreasing temperature below 150 K, and this could be associated with the disorder present in

the film structure. The metallic character disappeared in films prepared from mixtures with 1:3 molar ratio (Figure 5a). These observations are consistent with the results of Π - a isotherms and X-ray diffraction. In Figures 5b and 5c, the temperature variation of the dc resistance of LB films of C_{20} + BEDO-TTF and C_{22} + BEDO-TTF is shown. LB films prepared from a C_n + BEDO-TTF mixture with a 1:1 molar ratio are more resistive than films deposited from a mixture with molar ratio of 1:2. Moreover, the temperature (T_a) at which the slope of the R_s - T curve changes sign shifts toward lower temperatures for the films deposited from a 1:2 molar ratio mixture. However, the difference in sheet resistance ($R_{s(1:1)} - R_{s(1:2)}$) and ΔT_a ($T_{a(1:1)} - T_{a(1:2)}$) decreases with increasing alkyl chain length.

For all the LB films prepared from C_n + BEDO-TTF mixtures with 1:2 molar ratio, R_s increases remarkably in the temperature range of 150–300 K. This means that without the disorder effects below 150 K the sheet resistance would extrapolate to values close to zero as is observed in single crystals of BEDO-TTF-based salts.^{24,25} The room temperature resistivity value for single crystals of the polyoxometalate-containing radical salt of BEDO-TTF is reported as $0.027 \Omega\cdot\text{cm}$ and found to gradually decrease with the decreasing temperature, reaching a value of $0.001 \Omega\cdot\text{cm}$ at 2 K.²⁵ For these crystals, the temperature dependence of the resistivity is found to be linear above 200 K and quadratic below 200 K. The value of the resistivity and its thermal variation correlate with the structural properties of the compound as suggested by the previous studies on radical cation salts based on BEDO-TTF.^{24–27}

SUMMARY

In conclusion, the structural and consequently the electrical properties of the LB films composed of BEDO-TTF and fatty acid were found to be sensitive to the concentration of BEDO-TTF molecules in the starting C_n + BEDO-TTF mixture. This dependence was further studied by systematically varying the alkyl chain length of the fatty acid molecules. The molecules with long alkyl chain were observed to support a C_n + BEDO-TTF bilayer structure at the air/water interface even at relatively low concentration of BEDO-TTF in the C_n + BEDO-TTF mixture (i.e., for a 1:1 molar ratio). The in-plane area occupied by one BEDO-TTF remains roughly equal to that of one fatty acid molecule in the C_n + BEDO-TTF bilayer for all molar ratios. However, for all three fatty acids the concentration of defects in the LB film decreased when passing from 1:1 to 1:2 molar ratio in the starting mixture; the latter systematically gave rise to a more ordered structure and better conductive properties of the LB films. This suggests that the value of the resistivity and its temperature dependence is determined by the structural order, which in turn is determined by the C_n :BEDO-TTF ratio in the mixture from which the LB films are prepared.

ASSOCIATED CONTENT

Supporting Information

Π - a isotherms of Langmuir films of pure C_{20} and C_{20} + BEDO-TTF mixtures with different molar ratios, Π - a isotherms of Langmuir films of pure C_{22} and C_{22} + BEDO-TTF mixtures with different molar ratios, and the XRD pattern of a Langmuir–Blodgett film deposited from pure C_{18} . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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